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PAPER

Supramolecular assemblies involving metal–organic ring interactions: heterometallic Cu(II)–Ln(III) two-dimensional coordination polymers†

Konstantis F. Konidaris,^a Christine N. Morrison,^a John G. Servetas,^b Matti Haukka,^c Yanhua Lan,^d Annie K. Powell,^{ad} John C. Plakatouras^b and George E. Kostakis^{*a}

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Three isostructural two-dimensional coordination polymers of the general formula $[\text{Ln}_2(\text{CuL})_3(\text{H}_2\text{O})_9] \cdot 5.5\text{H}_2\text{O}$, where Ln = La (**1**), Nd (**2**), and Gd (**3**), have been synthesized and isolated from aqueous solutions and their single-crystal structures determined by X-ray diffraction. The supramolecular interaction between the non-aromatic metallorings plays an important role in stabilizing the structure of these compounds. The thermal stability, reversible solvent uptake, electronic properties and magnetic studies of these compounds are also reported.

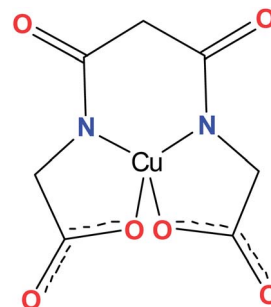
Introduction

During the last few decades, chemists have been hunting for novel compounds possessing both unique supramolecular structures and applicable properties.^{1,2} Multifunctional materials, such as huge coordination clusters with interesting magnetic properties³ or nanoporous coordination polymers with energy applications,⁴ have been the “heavyweight papers” in the stock market of coordination chemistry, attracting the attention of an increasing number of scientists. Several types of interactions have been employed for the synthesis of these interesting materials, including coordination bonds,⁵ hydrogen bonds,⁶ π – π stacking,⁷ halogen bonds,⁸ lone pair– π interactions, *etc.*⁹ There are several useful synthetic strategies for the synthesis of such kinds of materials and it is now well established that the metal–ligand (ML) approach is one of the most successful.¹⁰ A literature survey reveals a plethora of examples with MLs,¹¹ although it is worth noting that in most cases, when chemists target MLs in which the metal centre possesses an unsaturated environment, the organic ligands that have been utilized contain robust aromatic scaffolds.¹²

As part of our ongoing project to utilize pseudo-peptidic ligands¹³ for the synthesis of multifunctional materials, we have selected to study the coordination abilities of a non-aromatic,

water-friendly organic ligand, namely, malonamide-*N,N'*-diacetic acid (LH_4).¹⁴ This ligand can be chelated to a square planar Cu^{II} centre to produce two five- and one six-membered chelated rings, resulting in an almost planar dianionic ML (Scheme 1), in which the axial positions of the Cu^{II} centre are not occupied. Interestingly, we have found that almost planar MLs, that do not contain any aromatic scaffolding, can be stacked in a π – π stacking fashion through the five- and six-membered chelated rings. This type of supramolecular interaction, named as Metal–Organic Ring interaction (MORi),¹⁴ is similar to what is described by Calvin and Wilson in the structure of $\text{Cu}(\text{acac})_2$ in terms of “metalloaromaticity”,¹⁵ and to the best of our knowledge this example is the first one involving rings that are non-aromatic.¹⁶

Having first in mind the stacking arrangement of this ML and second the several oxygen atoms that are able to bond to other metal centres, we have now turned our attention to the synthesis of multidimensional compounds. In this study, we present the synthesis and structural characterization of three isostructural two-dimensional (2D) coordination polymers formulated as $[\text{Ln}_2(\text{CuL})_3(\text{H}_2\text{O})_9] \cdot 5.5\text{H}_2\text{O}$, where Ln = La (**1**), Nd (**2**), and Gd



Scheme 1 The almost planar dianionic metalloligand.

^aInstitute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-mail: George.Kostakis@kit.edu; Tel: +49-721 608-28920

^bDepartment of Chemistry, University of Ioannina, 451 10 Ioannina, Greece

^cDepartment of Chemistry, University of Eastern Finland, P.O. Box 111, FIN-80101 Joensuu, Finland

^dInstitute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstrasse 15, D-76131 Karlsruhe, Germany

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(3). The single-crystal X-ray structural analyses of all compounds reveal, as anticipated, supramolecular extended architectures generated by MOR interactions. The thermal stability, reversible solvent uptake, electronic and magnetic properties of these compounds have been studied.

Experimental

Materials and methods

All metal salts were purchased from Aldrich Chemicals. Organic solvents, KBr and BaSO₄, were purchased from Merck. The elemental analyses (C, H, and N) were carried out at the Institute of Inorganic Chemistry, Karlsruhe Institute of Technology using an Elementar Vario EL analyzer. Fourier transform IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr discs. UV/Vis diffuse reflectance spectra (DRS) were recorded on a Perkin-Elmer UV/Vis/NIR Spectrometer Lambda 900 with a BaSO₄ standard. X-Ray powder diffraction patterns for all compounds were measured at room temperature using a Stoe STADI-P diffractometer with a Cu-K α radiation at the Institute of Nanotechnology, Karlsruhe Institute of Technology.

Synthesis of [Ln₂(CuL)₃(H₂O)₉]·5.5H₂O

The same procedure was employed to prepare all complexes; hence, only compound **1** is described here in detail. Solid Cu(NO₃)₂·4H₂O (0.115 g, 0.5 mmol) was added to a stirred solution of LH₄ (0.109 g, 0.50 mmol) and Na₂CO₃ (0.053 g, 0.50 mmol) in H₂O (30 mL). The reaction mixture was stirred for 15 min, and then solid La(NO₃)₃·xH₂O (0.155 g, 0.50 mmol) was added gradually. The resulting dark blue solution was filtered and allowed to slowly evaporate at room temperature. After three days, magenta blocks of **1** were obtained in 65% yield. Crystals

were collected by filtration under vacuum, washed with H₂O (2 × 5 mL) and Et₂O (5 mL) and dried in air. Elemental analysis (%) calcd for La₂Cu₃C₂₁H₄₇N₆O_{32.5}: C 18.32, H 3.45, N 6.13; found: C 18.40, H 3.43, N 6.20. IR (KBr, cm⁻¹): 3410 (s, b), 1587 (s), 1424 (s), 1373 (s), 1293 (m), 1269 (m), 1092 (m), 1014 (w), 937 (m), 733 (m), 587 (m), 555 (m), 524 (m), 420 (m). Similarly for **2**, yield 60%, elemental analysis (%) calcd for Nd₂Cu₃C₂₁H₄₇N₆O_{32.5}: C 18.24, H 3.43, N 6.08; found: C 18.30, H 3.48, N 6.10. IR (KBr, cm⁻¹): 3410 (s, b), 1587 (s), 1424 (s), 1373 (s), 1293 (m), 1269 (m), 1092 (m), 1014 (w), 937 (m), 733 (m), 587 (m), 555 (m), 524 (m), 420 (m). Similarly for **3**, yield 62%, elemental analysis (%) calcd for Gd₂Cu₃C₂₁H₄₇N₆O_{32.5}: C 17.90, H 3.36, N 5.97; found: C 18.00, H 3.33, N 6.00. IR (KBr, cm⁻¹): 3410 (s, b), 1587 (s), 1424 (s), 1373 (s), 1293 (m), 1269 (m), 1092 (m), 1014 (w), 937 (m), 733 (m), 587 (m), 555 (m), 524 (m), 420 (m).

Single crystal X-ray data collection and structure determination

Experimental details of the X-ray analyses are provided in Table 1. The isomorphous crystals of **1–3** were immersed in cryo-oil mounted in a Nylon loop, and measured at a temperature of 105 K. The X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer using Mo-K α radiation (λ = 0.71073 Å). The *Denzo–Scalepack*^{17a} program package was used for cell refinements and data reductions. The structures were solved by direct methods using the *SHELXS-97*^{17b} program with the *WinGX*^{17c} graphical user interface. A semi-empirical absorption correction (*SADABS*^{17d} or *SORTAV*^{17e}) was applied to all data. Structural refinements were carried out using *SHELXL-97*.^{17b} The crystal of **1** was refined as a twin using the twin matrix [0.375 –0.420 0.625 0 –1 0 1.375 –0.420 –0.375] and the BASF was refined to 0.16136. In all structures, the water molecules, O13 and O14, are disordered over two sites. Furthermore, in **1** the disordered oxygen atoms, O13A and O13B as well as O14A and O14B,

Table 1 Crystal data and structure refinement parameters for compounds **1–3**

	1	2	3
Empirical formula	C ₄₂ H ₉₄ Cu ₆ La ₄ N ₁₂ O ₆₅	C ₄₂ H ₉₄ Cu ₆ N ₁₂ Nd ₄ O ₆₅	C ₄₂ H ₉₄ Cu ₆ Gd ₄ N ₁₂ O ₆₅
fw	2744.17	2765.49	2817.53
Temperature/K	105(2)	105(2)	105(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073
Cryst. syst.	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	11.291(2)	11.190(2)	11.0485(3)
<i>b</i> /Å	13.235(3)	13.181(3)	13.1016(3)
<i>c</i> /Å	15.436(3)	15.356(3)	15.4028(3)
α/deg	73.80(3)	73.70(3)	73.203(2)
β/deg	72.74(3)	72.87(3)	72.574(2)
γ/deg	79.37(3)	79.78(3)	79.917(2)
<i>V</i> /Å ³	2102.3(7)	2066.5(7)	2026.92(8)
<i>Z</i>	1	1	1
$\rho_{\text{calc}}/\text{Mg m}^{-3}$	2.168	2.222	2.308
μ (Mo K α)/mm ⁻¹	3.595	4.102	4.893
No. reflections	7436	36 216	39 481
Unique reflections	7436	9405	9260
GOF (<i>F</i> ²)	1.116	1.044	1.063
<i>R</i> _{int}	0.0660	0.0484	0.0481
<i>R</i> 1 ^a (<i>I</i> ≥ 2 σ)	0.0517	0.0345	0.0360
<i>wR</i> 2 ^b (<i>I</i> ≥ 2 σ)	0.1474	0.0832	0.0748
CCDC number	835270	835271	835272

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

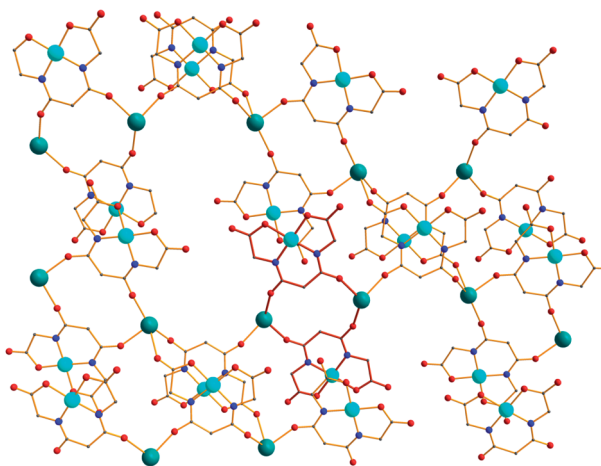
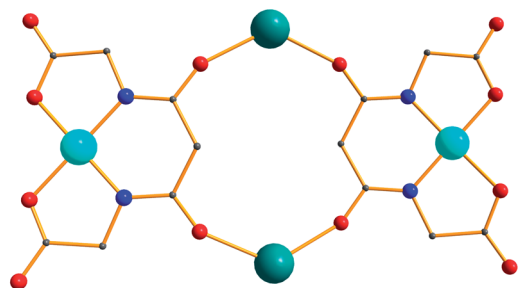
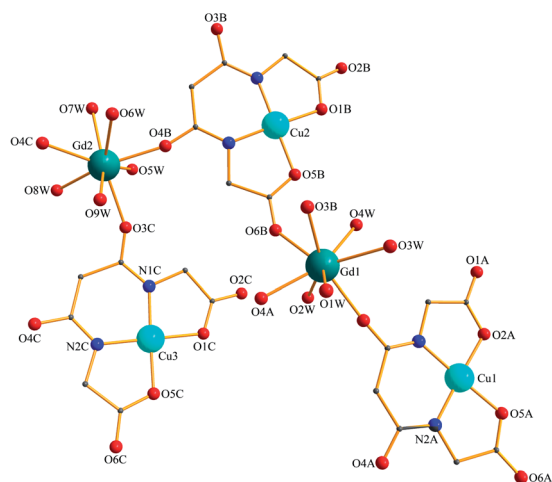
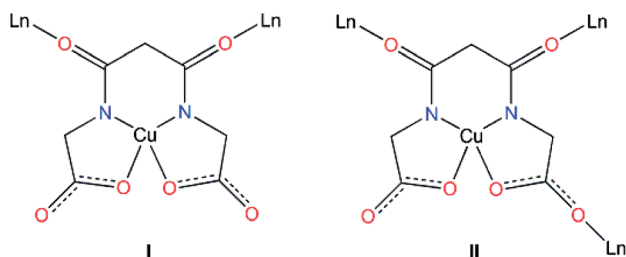


Fig. 1 (top) Molecular structure of **3**. (middle) The dicationic dimeric unit formulated as $\{[\text{Gd}(\text{CuL})]_2\}^{2+}$. (bottom) The 2D layer formed in **3**, emphasizing the dicationic dimeric units $\{[\text{Gd}(\text{CuL})]_2\}^{2+}$. H atoms have been omitted for clarity.



Scheme 2 The two coordination modes of the ML found in **3**: mode I for **A** and **C** and mode II for **B**.

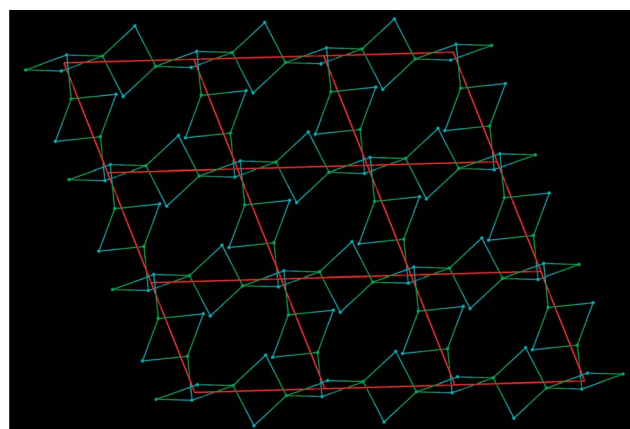


Fig. 2 The topological representation of the 2D coordination polymer possessing a *fes* topology.

were refined with equal anisotropic displacement parameters. Also in all structures, one of the water molecules, O15, was partially lost and refined with an occupancy of 0.5. The H_2O hydrogen atoms were located from the difference Fourier map or by using the *HYDROGEN*¹⁷ program and then constrained to ride on their parent atom with $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{parent atom})$. Other hydrogens were positioned geometrically and were also constrained to ride on their parent atoms, with $\text{C-H} = 0.99 \text{ \AA}$, and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{parent atom})$. Due to the disorder, twinning, and different treatment of H-atoms some H...H contacts were slightly shorter than the average H...H contact.[†]

Results

Crystal structure studies reveal that all compounds are isomorphous (Table 1); thus, only the structure of **3** will be further described. The 2D coordination polymer is constructed from almost linear dianionic ML nodes connected by Ln spacers (Fig. 1). The powder XRD diffraction pattern (Fig. S1[†]) indicates the phase purity of all compounds. The asymmetric unit contains two Gd^{III} cations, three dianionic MLs and 14.5 water molecules (9 ligated and 5.5 lattices). Each Cu^{II} ion is embraced (CuN_2O_2 coordination) by the organic ligand, forming a dianionic ML.

There are three crystallographically independent dianionic CuL units in **3**, named hereafter as **A**, **B** and **C**, for Cu1, Cu2 and Cu3, respectively. **A** and **C** are ligated through their amidic carbonyls to two Gd^{III} ions (Scheme 2, mode I), and **B** is ligated to two Gd^{III} ions through the carbonyl oxygens as well as to one Gd ion through one carboxylate oxygen atom (Scheme 2, mode II). The coordination number of both Gd^{III} ions is eight; both lanthanides are ligated to three carbonyl oxygen atoms of three different MLs, and Gd1 is ligated to an additional dianionic unit through a carboxylate oxygen atom.

The coordination sphere of Gd1 and Gd2 is completed with four and five water molecules, respectively. The coordination environment of each Gd^{III} can be best described in terms of a square antiprism, while the copper ions display a square planar geometry. It is worth noting that a comparison of the bond distances of all compounds (Tables S1–S3[†]) shows

Table 2 Abbreviation of the nine planar rings found in **1** along with deviation (Å) from the plane

Cg(1)/dev/Å	Cu(1)/−0.011(4)	O(2A)/−0.017(4)	C(1A)/0.011(11)	C(2A)/−0.018(12)	N(1A)/0.018(10)	
Cg(2)/dev/Å	Cu(1)/−0.041(4)	O(5A)/0.005(9)	C(7A)/0.033(11)	C(6A)/−0.058(12)	N(2A)/0.061(10)	
Cg(3)/dev/Å	Cu(2)/−0.002(4)	O(1B)/−0.041(9)	C(1B)/0.068(11)	C(2B)/−0.069(12)	N(1B)/0.044(10)	
Cg(4)/dev/Å	Cu(2)/−0.041(4)	O(5B)/0.007(9)	C(7B)/0.029(12)	C(6B)/−0.054(11)	N(2B)/0.059(10)	
Cg(5)/dev/Å	Cu(3)/−0.020(4)	O(1C)/−0.024(9)	C(1C)/0.059(12)	C(2C)/−0.071(12)	N(1C)/0.056(10)	
Cg(6)/dev/Å	Cu(3)/0.005(4)	O(5C)/0.016(9)	C(7C)/−0.031(12)	C(6C)/0.034(12)	N(2C)/−0.025(10)	
Cg(7)/dev/Å	Cu(1)/−0.040(4)	N(1A)/0.062(9)	C(3A)/−0.021(11)	C(4A)/−0.040(11)	C(5A)/0.062(11)	N(2A)/−0.021(9)
Cg(8)/dev/Å	Cu(2)/−0.011(4)	N(1B)/0.085(9)	C(3B)/−0.083(10)	C(4B)/0.007(11)	C(5B)/0.068(11)	N(2B)/−0.065(9)
Cg(9)/dev/Å	Cu(3)/0.025(4)	N(1C)/0.015(10)	C(3C)/−0.079(11)	C(4C)/0.103(11)	C(5C)/−0.062(11)	N(2C)/−0.002(10)

a delocalization of the carboxylate groups of **3**, in contrast to our previous findings (Scheme 2).¹⁴

A better overview of the crystal structure of **3** shows that two dicationic dimeric units formulated as $\{\text{[Gd(CuL)}_2\}_2^{2+}$ (Fig. 1, middle) are linked through the carbonyl oxygen atoms of two dianionic MLs, **A** and **C** (Scheme 2, mode II), to form one-dimensional (1D) chains. In this motif, the dimeric units are situated in the inner part of the chain and the MLs are the “wings” of the chain. The 1D chains run along the bisection of the $a0b$ angle and interact with each other through the carboxylate oxygen atoms of the latter ML that is ligated to every Gd1 centre. Compound **3** is extended to two dimensions parallel to the bisect of the $a0c$ angle (Fig. 1, bottom), through the carboxylate oxygen atoms, causing the formation of thick layers.

Following the traditional way of analyzing the topology of **1–3**, the 2D network can thus be described in terms of a binodal 3-connected net possessing **fes** topology (Fig. 2).¹⁸

The square planar geometry of each Cu^{II} centre dictates that each ML adopt a planar conformation. The three crystallographically independent MLs are almost planar in all three compounds. For example, for compound **1** (Table 2) there are no big differences for **A/C** and **B**, respectively, despite the different coordination modes (Scheme 2). It is worth noting that the axial positions of each Cu^{II} are not occupied; however, the structural analysis shows that the three planar MLs are within the range of 3.280 to 3.8 Å, similar to that found in π – π stacking interactions and in graphite.^{7a} In the present compounds, this stacking arrangement of the planar ML has a repeating motif, which can be described as **A**···**C**···**C**···**A**···**B**···**B**, forming helices running parallel to the bisect of the $b0c$ angle with a pitch of 22.279 Å. The MLs are rotated almost 120° angles in **A**···**C**, **C**···**A**, **A**···**B** and **B**···**A** and 180° angles in **C**···**C** and **B**···**B**, respectively. The minimum distances between the least square planes are 3.382 Å, 3.354 Å and 3.280 Å for **1**, **2** and **3**, respectively, while the minimum Cu–centroid distances are 3.389 Å, 3.368 Å and 3.350 Å for **1**, **2** and **3**, respectively. Thus, as shown in Fig. 3 (bottom) and Table 3, the thick layers of the 2D coordination polymers are packed through MORi to the third dimension forming a supramolecular 3D architecture.

The diffuse reflectance spectra (DRS) of all compounds (Fig. 4) show a broad peak in the area of 400–700 nm, which can be attributed to a square planar conformation of the Cu^{II} centers,^{19a} while the peaks in the area below 1000 nm for **2** can be attributed to typical spectra for Nd^{III} (581: $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^4\text{G}_{7/2}$, shoulder at 684: $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{9/2}$, 744: $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{7/2}$, $^4\text{S}_{3/2}$, 801 shoulder: $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$, $^2\text{H}_{9/2}$, 886: $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$).^{19b}

To probe the nature of magnetic exchange interactions in the compounds, variable-temperature magnetic susceptibility data in both DC and AC mode were collected. The molar susceptibility data of **1–3** were calculated using a doubled formula weight, corresponding to the molecule in each asymmetric unit containing the building block, $[\text{Ln}_2(\text{CuL})_3(\text{H}_2\text{O})_9] \cdot 5.5\text{H}_2\text{O}$. For all the compounds, the AC susceptibility was checked but showed no out-of-phase signal above 1.8 K and no frequency dependence of the in-phase component. A plot of DC susceptibility (χT vs. T) collected under an applied DC field of 1000 Oe is shown in Fig. 5.

Upon lowering the temperature, the χT product of **1** is constant until 20 K and then decreases down to 1.8 K, suggesting the presence of antiferromagnetic (AF) interactions. The χT product at high temperature almost follows a Curie law and is nearly temperature independent, indicating the weak nature of the interaction. This is consistent with the structure having very weak intramolecular magnetic interactions between Cu ions mediated through $\{\text{[La(CuL)}_2\}_2^{2+}$ spacers. An attempt was made to fit the magnetization M using the sum of six Brillouin functions of $S = 1/2$ and $g = 2.2$ (Fig. S2†); however, the experimental M curve is offset low compared with the calculated curve, confirming that the AF nature is probably due to MOR interactions, as observed in the layers. For Nd compound **2**, the χT product follows a monotonic decrease upon lowering the temperature from RT down to 1.8 K, indicating that the Cu–Nd interactions are dominantly AF. However, for the Gd compound, the χT product stays almost constant before increasing to 50.0 cm³ K mol^{−1} at 1.8 K. This behaviour suggests that the Cu–Gd interactions are ferromagnetic. We can subtract the molar susceptibility of the diamagnetic La analogue from **2** and **3** to give suitably adjusted plots (Fig. S3†) in order to assess the nature of Cu–Ln interactions. The profile of the adjusted χT vs. T plot confirms the ferromagnetic nature of the commonly observed Cu–Gd interactions.²⁰ A Curie–Weiss fit of the adjusted χT vs. T curve above 30 K (Fig. S3†) leads to $C = 30.6$ cm³ K mol^{−1} and $\theta = 1.7$ K. The small Weiss constant indicates that the Cu–Gd interaction is weak; however, it is dominant in compound **3** and overwhelmingly present in Cu···Cu MOR interactions.

Thermogravimetric analyses on as-isolated crystalline samples of **1–3** (Fig. 6, top) show a weight loss from 50 to 190 °C, corresponding to the partial loss of water molecules. The partially dehydrated products are stable up to 235 °C. The second weight loss from 240 to 400 °C corresponds to the framework collapse, and after 400 °C, all compounds start to decompose fully. As a possible explanation for the final residue, we propose a mixture of Ln₂O₃ and CuO (obsd 64.74%, calcd 64.88% for **1**; obsd 65.67%, calcd 65.93% for **2**; and obsd 68.64%, calcd 68.88%

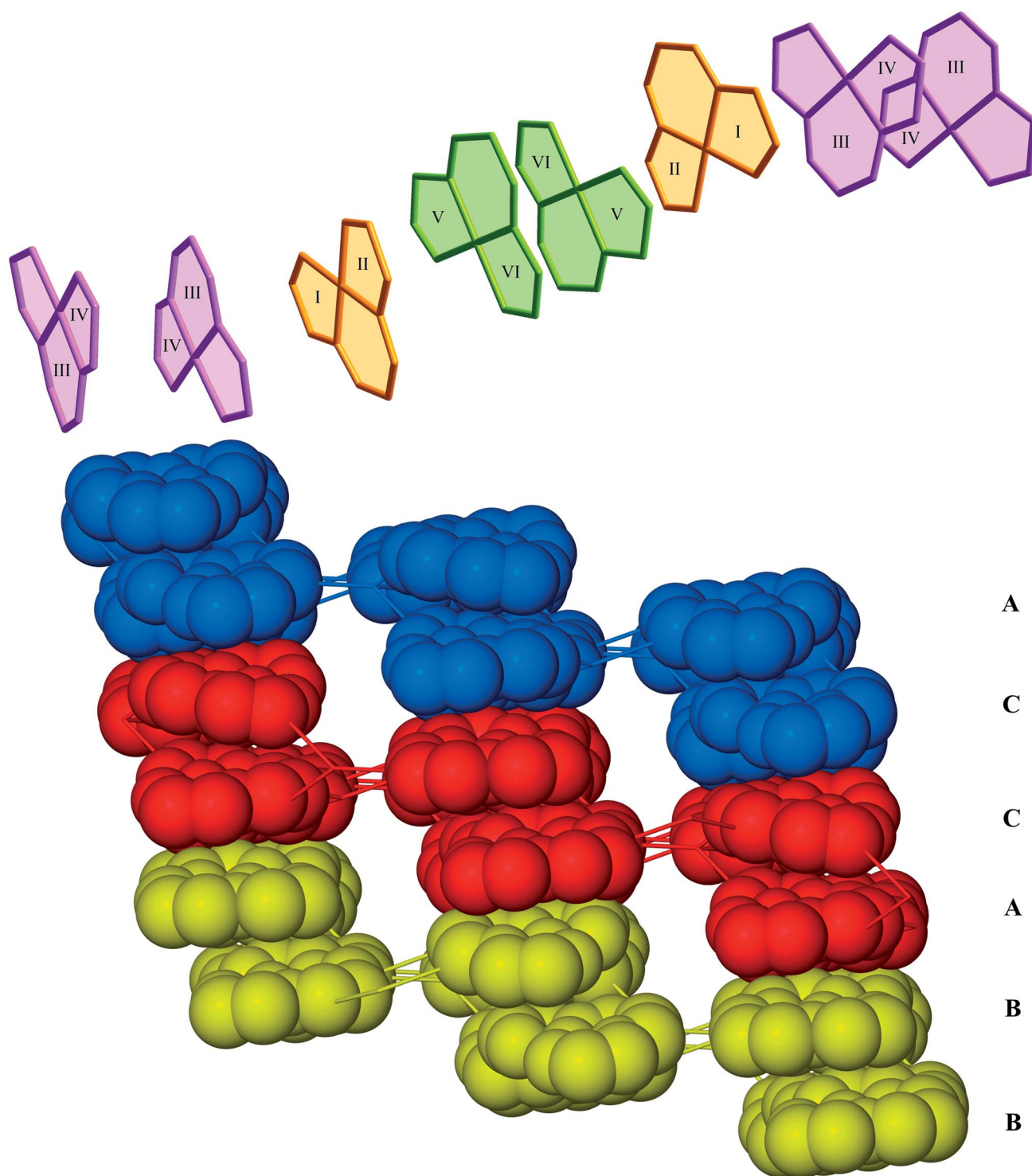


Fig. 3 (top) The MOR interactions found in **3**. A part motif of $\mathbf{B} \cdots \mathbf{B} \cdots \mathbf{A} \cdots \mathbf{C} \cdots \mathbf{C} \cdots \mathbf{A} \cdots \mathbf{B} \cdots \mathbf{B}$ is presented herein. Color code of MLs: A orange; B green; and C purple. Hydrogen atoms, water molecules, the carboxylate and carbonyl groups are omitted for clarity. Numbering of the rings is in agreement with Table 3. (bottom) The 3D supramolecular architecture found in **1–3**. A part motif of $\mathbf{A} \cdots \mathbf{C} \cdots \mathbf{C} \cdots \mathbf{A} \cdots \mathbf{B} \cdots \mathbf{B}$ is presented in a sphere packing representation of compound **3** in order to emphasize the supramolecular interaction. Three different 2D layers (blue, red, and yellow) are extended to the third dimension through the MOR interactions.

for **3**). Reversible solvent uptake either as lattice molecules²¹ or acting as bridges^{13a} is widely seen in coordination chemistry. It is also known that solvents are not only important to structural assemblies but also to structural transformations.²² The

transformations associated with thermal desolvation and resolvation were probed using powder XRD measurements. Upon heating the crystals of compound **1** at 125 °C in a high vacuum overnight, lattice water molecules were removed and the

Table 3 Selected Metal–Organic Ring interactions (MORi) with Cg–Cg distances for **1**, **2** and **3**

	MORi ^a	Distance/Å
1 (La)	Ring II···Ring V	3.492
	Ring I···Ring III	3.482
	Ring III···Ring IV	3.382
	Ring V···Ring VI	3.554
2 (Nd)	Ring II···Ring V	3.494
	Ring I···Ring III	3.354
	Ring III···Ring IV	3.543
	Ring V···Ring VI	3.500
3 (Gd)	Ring II···Ring V	3.441
	Ring I···Ring III	3.474
	Ring III···Ring IV	3.280
	Ring V···Ring VI	3.533

^a Ring I (Cu1)(O2A)(C1A)(C2A)(N1A); Ring II (Cu1)(O5A)(C7A)(C6A)(N2A); Ring III (Cu2)(N1B)(C3B)(C4B)(C5B)(N2B); Ring IV (Cu2)(N2B)(C6B)(C7B)(O5B); Ring V (Cu3)(N2C)(C6C)(C7C)(O5C); and Ring VI (Cu3)(O1C)(C1C)(C2C)(N1C). Ring III is six-membered, while I, II, IV, V and VI are five-membered.

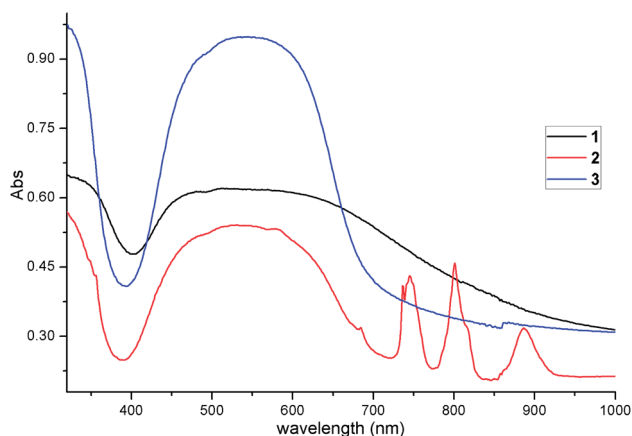


Fig. 4 The diffuse reflectance spectra (DRS) for compounds **1–3**.

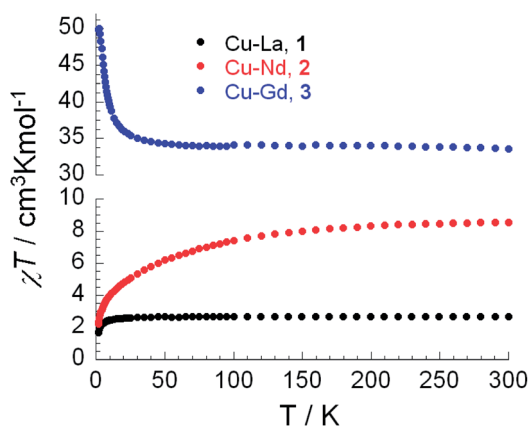


Fig. 5 Plots of χT vs. T of **1–3** under an applied DC field of 1000 Oe.

dehydrated framework is obviously different from the original material according to the PXRD patterns, indicating a structural transformation during this process.²² It should be noted that coordination polymers with similar structures may show

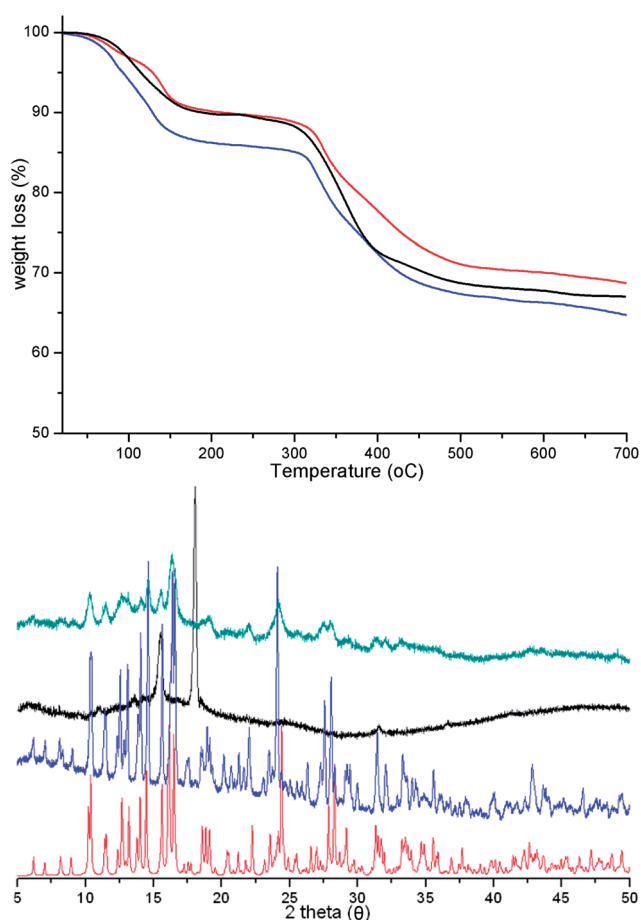


Fig. 6 (top) A TGA graph of compounds **1** (blue), **2** (black) and **3** (red), (bottom) Powder XRD patterns for compound **1**: theoretical (red), experimental (blue), heated (black) and rehydrated (light blue).

different dehydrated/rehydrated behaviours;²³ however, when the partially dehydrated compound was suspended in an aqueous solution, a less crystalline material was isolated (Fig. 6 (bottom), S4 and S5†) having a similar identity in comparison with the initial structure.

Discussion

In this work, we have extended our systematic study on the coordination abilities of malonamide-*N,N'*-diacetic acid, emphasizing the *in situ* synthesis of MLs for the isolation of multidimensional compounds. As it was anticipated from our previous work,¹⁴ in compounds **1–3** Cu^{II} adopts a square planar conformation as a result of the chelation (rather than bridging) mode of ligand. This results in the formation of three similar and essentially planar ML units that are linked through coordination bonds to Ln centers. This, in turn, leads to the formation of a 2D coordination polymer. The MLs are stacked *via* MORi to give a 3D supramolecular architecture. A literature survey¹⁶ shows that similar structural motifs exist;²⁴ however, to the best of our knowledge, the motif presented in our compounds is the first that arises where the chelating organic ligands do not possess aromatic rings. It is also worth noting that the square planar geometry of the Cu^{II} centre is in this case what can be described as a truly square planar case. Most examples of square planar

Cu^{II} sites in the literature with what can be regarded as flexible ligands have Cu^{II} ions in environments where relatively distant axial ligands are in fact present and can be regarded as extreme cases of the Jahn–Teller distortion of the octahedral d⁹ cation. In the compounds here, there are no nearby ligands to fulfil this role. As is well documented, the expectation for the d⁹ configuration is that the orbitals will be split by the coordination sphere geometry to lift the degeneracy of the d_{x²−y²} and d_{z²} orbitals, but this is usually achieved by adopting the 4 + 2 distortion of the octahedral case or through a 5-coordinate geometry. Examples of the true square planar geometry for Cu^{II} ions are largely limited to cases where the geometry is imposed by a 4-donor macrocyclic ligand such as a porphyrin or phthalocyanine.^{19a} In fact, the similarities to Cu^{II}/phthalocyanine systems are striking.

In other words, with this work we would like to highlight that with the careful selection of an organic ligand and a metal centre that favors the square planar geometry, it is possible to reproduce structural motifs with stacking character. For instance, a structural motif similar to MORi, but not recognized, has been recently reported elsewhere.²⁵ The structural evidence presented herein emphasizes the existence of a new supramolecular interaction.

Conclusions

In conclusion, we have presented the synthesis and characterization of three isostructural 2D compounds that are thermally stable up to 235 °C. We have shown that the malonamide-*N,N'*-dicarboxylic acid is suitable for the *in situ* synthesis of MLs and the synthesis of new kinds of 2D coordination polymers. Magnetic studies show weak ferromagnetic interactions for compound 3. The 2D coordination polymers are held to form a 3D supramolecular structure through MOR interactions. The structural evidence for this presented here shows that the MOR interaction adds a new dimension in the field of supramolecular chemistry which may be expected to be found in other systems containing metal ions in unexpected coordination environments for their electron configurations as we found here for the Cu^{II} ion.

The next targets of our systematic study are: (a) to theoretically investigate this type of interaction,²⁶ (b) to study the influence of lanthanide radii on the shape of the final product, (c) to study the influence of highly anisotropic lanthanides such as Dy^{III}, Tb^{III}, and Ho^{III} on the magnetic properties, (d) to study the catalytic properties of those materials on cyclopropanation reactions,²⁷ (e) to examine the capabilities of depositing such planar 2D components on graphene, due to the stacking character of those materials, and (f) to examine the electric-conductive properties of those materials.²⁸

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